

# OFFICIAL FILE COPY

AFWAL-TR-81-4100

ADA 111 393



## PROPERTIES OF BLENDS OF POLYPHENYLSULFONE AND ACETYLENE TERMINATED REACTIVE PLASTICIZER

Ivan J. Goldfarb

Polymer Branch  
Nonmetallic Materials Division

Dr. S. Sikka  
University of Dayton Research Institute  
Dayton, Ohio

November 1981

Final Report for Period October 1979 to June 1980

Approved for public release; distribution unlimited.

MATERIALS LABORATORY  
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

20040223007

Best Available Copy

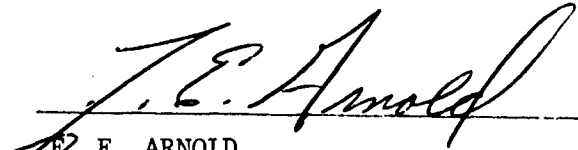
OFFICIAL FILE COPY


NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
F. E. ARNOLD  
Project Scientist

  
R. L. VAN DEUSEN, Chief  
Polymer Branch  
Nonmetallic Materials Div.

FOR THE COMMANDER

  
F. D. CHERRY, Chief  
Nonmetallic Materials Div.

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/MLBP, W-PAFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-81-4100	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PROPERTIES OF BLEND OF POLYPHENYLSULFONE AND ACETYLENE TERMINATED REACTIVE PLASTICIZER		5. TYPE OF REPORT & PERIOD COVERED Final Report October 1979-June 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Steven S. Sikka Ivan J. Goldfarb		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Laboratory Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62102F/2419/04, 24190415
11. CONTROLLING OFFICE NAME AND ADDRESS Materials Laboratory Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE November 1981
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release, distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polyphenylsulfone, acetylene terminated sulfone, reactive plasticizer, polyblends, thermoplastic matrix resins.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polyblends of polyphenylsulfone (PPS) and reactive plasticizer (acetylene terminated sulfone) have been considered as matrix resins for graphite reinforced composites. The thermoplastic polyphenylsulfone provides high glass transition temperature and therefore high end-use temperature while the reactive plasticizer-acetylene terminated sulfone (ATS) lowers the glass transition temperatures and the viscosities of the blends for the purpose of improved processing conditions. Since ATS contains reactive acetylene functional groups, it reacts and becomes dormant in the system.		

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Blends of polyphenylsulfone and reactive plasticizer have been prepared in weight percent compositions of 90 PPS/10 ATS, 80 PPS/20 ATS, 70 PPS/30 ATS, and 60 PPS/40 ATS. These were cast from chloroform solvent yielding clear films. The calculated and measured refractive indices of PPS/ATS are about the same and therefore light scattering studies of polyblends have not shown any phase separation of PPS and ATS. Transmission electron microscopy on microtomed specimens of PPS/ATS blends indicates a possibility of phase-separation of the two components but it needs further investigation. Cure studies of these blends have shown retention of about 14% solvent which has additional influence in lowering the Tg of the blends. The dynamic mechanical properties of polyblends show broad  $\tan \delta$  peaks in the uncured state while the Tg of cured PPS/ATS polyblends equals that of PPS by itself. Addition of ATS to PPS thus lowers the Tgs and the viscosities which in turn lowers the temperature requirement for processing.

The ATS in PPS/ATS reacts/crosslinks on curing, providing better solvent resistance of PPS/ATS blends than PPS polymer alone.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Materials Laboratory Project Scientist. Co-authors were Dr. S. Sikka, University of Dayton Research Institute and Dr. I. J. Goldfarb, Air Force Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from October 1979 to June 1980.

The authors wish to thank Mr. E. J. Soloski for the determination of glass transition temperatures.

## TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II EXPERIMENTAL	2
1. Materials	2
2. Preparation of Polyblends	2
3. Dynamic Mechanical Properties and Glass Transition Temperatures	3
4. Viscosity Measurements	3
5. Curing of Blends	3
6. Density Measurements	3
III RESULTS AND DISCUSSION	4
1. Compatibility of Polyblends	4
2. Curing of PPS/ATS Blends	27
3. Viscosity Measurements	29
4. Solvent/Chemical Resistance	29
IV CONCLUSIONS	35
REFERENCES	36

## LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	E* and Log Tan $\delta$ vs. Temperature Plot for Solvent Cast Polyphenylsulfone (PPS) Film	6
2	E* and Log Tan $\delta$ vs. Temperature Plot for 90 PPS/10 ATS Uncured Blend	7
3	E* and Log Tan $\delta$ vs. Temperature Plot for 80 PPS/20 ATS Uncured Blend	8
4	E* and Log Tan $\delta$ vs. Temperature Plot for 70 PPS/30 ATS Uncured Blend	9
5	E* and Log Tan $\delta$ vs. Temperature Plot for 60 PPS/40 ATS Uncured Blend	10
6	Log Tan $\delta$ vs. Temperature Plot for 90 PPS/10 ATS Uncured Film	12
7	E', E'', and Log Tan $\delta$ Plot of 80 PPS/20 ATS Uncured Blend	13
8	TGA Curve for 70 PPS/30 ATS Uncured Blend	14
9	TMA Scan of 80 PPS/20 ATS Uncured Blend	21
10	DSC Scan of 80 PPS/20 ATS Cured Blend	23
11	E', E'', and Log Tan $\delta$ vs. Temperature Plot for 80 PPS/20 ATS "Fully Cured" Blend	24
12	Plot of Tg's of Uncured and Cured Blends	25
13	DSC Scans of 80 PPS/20 ATS "Fully Cured" Blend	26
14	Superimposed IR Spectra of Uncured and Cured 80 PPS/20 ATS Blend	28
15	Viscosity vs. Temperature Plot for PPS Polymer Film. Test Frequency = 1.6 HZ	30
16	Viscosity vs. Temperature Plot for 80 PPS/20 ATS Uncured Blend. Test Freq. = 1.6 HZ	31
17	Viscosity vs. Temperature Plot for 70 PPS/30 ATS Uncured Blend. Test Freq. = 1.6 HZ	32

## LIST OF TABLES

TABLE		PAGE
1	Observed and Calculated Tg's of PPS/ATS Polyblends of Various Compositions	15
2	Cure Temperatures, Densities, and Weight Loss Data of PPS, ATS, 80 PPS/20 ATS and 70 PPS/30 ATS Polyblends	18
3	Glass Transition Temperatures of PPS and PPS/ATS Blends as Determined by DSC and TMA	20
4	Solvent Resistance of PPS and "Fully Cured" 80 PPS/20 ATS Polyblend	33



## SECTION I

### INTRODUCTION

Interest has been generated in using thermoplastics as matrix resins for graphite reinforced composites for advanced aerospace applications. The typical thermoplastics considered for such applications possess high glass transition temperatures to provide high end-use temperatures. Although thermoplastics provide potential ease in handling and forming, they do require high processing temperatures. In addition, thermoplastics are susceptible to solvent-induced crazing thus limiting their use for aircraft structures. Therefore, for successful applications of thermoplastic matrix resins, it is required that the processing temperatures be lowered while maintaining high end-use temperatures and solvent resistance be improved. This has been made possible by blending thermoplastics with reactive plasticizers which have been synthesized at the Air Force Wright Aeronautical Laboratories (Reference 1). The reactive plasticizer contains reactive acetylene terminated groups.

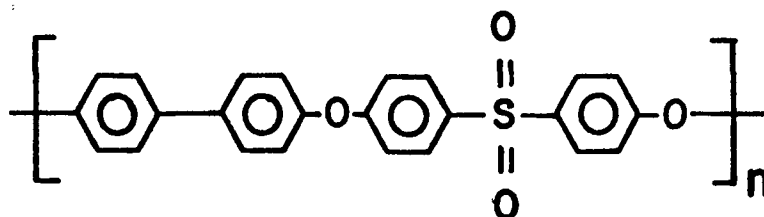
Like commercial diluents, the reactive plasticizers lower the glass transition temperatures by increasing the free volume and consequently lower the viscosities and processing temperatures. But unlike the commercial plasticizers and diluents, the reactive plasticizer undergoes a thermally initiated addition reaction/polymerization on processing and subsequent cure treatment, forming a crosslinked network structure without giving out any volatile reaction products. This type of molecular structure formed by the plasticizer is expected to provide better chemical resistance as opposed to leaching out of common plasticizers at elevated temperatures and their increased susceptibility to organic solvents.

## SECTION II

### EXPERIMENTAL

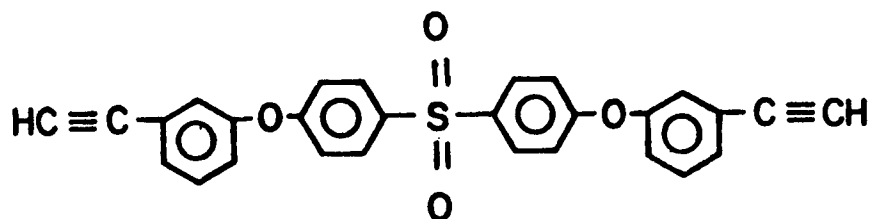
#### 1. MATERIALS

The thermoplastic used in the present study is Polyphenyl Sulfone, PPS (Radel TM, Union Carbide) having the following structure:



The Tg of PPS is 220°C.

The reactive plasticizer used in blending PPS is Acetylene Terminated Sulfone (ATS)<sup>1</sup> with the following chemical structure:



4', 4''-bis-(3-ethynylphenoxy)diphenyl sulfone (ATS)

The Tg of ATS is ~ 0°C.

#### 2. PREPARATION OF POLYBLENDS

PPS polymer was dried under vacuum at 150°C for two and one half hours as recommended by Union Carbide (Reference 2). The dried polymer and the ATS were dissolved in chloroform in such weight proportions as to yield 90% PPS/10% ATS, 80% PPS/20% ATS, 70% PPS/30% ATS, and 60% PPS/40% ATS blend compositions. Solutions of these blends were poured on glass plates

<sup>1</sup>This batch of ATS contained ATS 79.76% and 21.24% monovinyl ether of ATS, as described in Reference 1.

under the dry box and clear films were obtained by evaporation of solvent under nitrogen.

### 3. DYNAMIC MECHANICAL PROPERTIES AND GLASS TRANSITION TEMPERATURES

The dynamic moduli and glass transition temperatures of various polyblend compositions have been determined by Rheovibron Model DDV-II-C (automated by I-MASS) between -150 and 250°C at a heating rate of about 2°C/minute.

The glass transition temperatures were also determined by Differential Scanning Calorimeter (DuPont Model 990) and Thermal Mechanical Analyzer (DuPont Model 942) at a heating rate of 10°C/min.

### 4. VISCOSITY MEASUREMENTS

Viscosity measurements as a function of temperature were made on the Rheometrics RMS 7200 Mechanical spectrometer by placing the polyblend films between the preheated parallel plates and subjecting them to a low frequency (1.6 Hz) sinusoidal shearing rate.

### 5. CURING OF BLENDS

The PPS/ATS blend films were cured in a vacuum oven. The temperature was raised from ambient to 285°C in various stages to avoid foaming of films. The extent of cure was monitored by following the disappearance of the 3280  $\text{cm}^{-1}$  infrared band (acetylene C-H stretch).

### 6. DENSITY MEASUREMENTS

The densities of uncured and cured PPS/ATS blends were measured in a density gradient column filled with aqueous sodium bromide solution calibrated with density floats of precisely known densities. The densities were measured with an accuracy of  $\pm 0.001$  g/ml.

### SECTION III

#### RESULTS AND DISCUSSION

##### 1. COMPATIBILITY OF POLYBLENDS

The compatibility of polymer blends or polymer - polymer miscibility is generally based on the following criteria:

- Dissolution in a common solvent (i.e., no phase separation)
- Mechanical integrity
- Optical transparency
- A single relaxation peak in the dynamic mechanical measurements
- A single glass transition temperature
- Homogeneity of the structure in 50-100°A range

In the present case of PPS and ATS blends, their solutions in chloroform are clear and have shown no phase separation. The films cast from this solution are transparent and possess mechanical integrity. Very thin cast films of PPS and PPS/ATS blends show no light scattering. These films when viewed through optical microscope and scanned under scanning electron microscope, again, do not show any phase separation. This suggests that either the electron densities of two components in blends are about the same and/or the blends are compatible. The refractive indices of PPS and ATS are 1.7045 and 1.6585, respectively, as measured on the refractometer. These observed refractive indices correspond well to the calculated refractive indices of 1.6475 and 1.5999 for PPS and RPS, respectively. The calculated refractive indices are based on group contributions to molar refraction using the Vogel equation  $R_v = nM$  where  $R_v$  is the molar refraction and  $M$  the molecular weight of the repeat unit (Reference 3). Therefore, even if the two components were phase separating, it would be difficult to conclude from the light - scattering and optical microscopy data. Since the repeat units of the two components have similar chemical structure, it is possible that their

electron densities may also be similar, making it difficult to distinguish between the two phases. Several transmission electron micrographs have been obtained from microtomed specimens of pure PPS, pure ATS ("fully cured") and PPS/ATS uncured, and cured blends. Micrographs of these samples have also been obtained in TEM after staining the microtomed specimens (studied earlier) with Osmium tetra oxide. The TEM micrographs of solvent-cast PPS and fully cured ATS show smooth surfaces. However, the TEM micrographs of PPS/ATS blends, blended in any composition, show light color domains of 0.5 to 1  $\mu\text{m}$  dispersed in a darker matrix. These observations need to be further investigated and correlated with DSC, TMA, and dynamic mechanical data.

The dynamic mechanical measurements have been made on blends of various compositions in uncured and cured states. The extent and completion of cure have been determined from the infrared spectra. The dynamic mechanical spectrum of solvent-cast PPS film is shown in Figure 1. This figure shows the complex dynamic modulus and  $\tan \delta$  (plotted on a log scale) as a function of temperature. The modulus shows a single drop above 220°C which is the glass transition temperature of PPS. The log  $\tan \delta$  curve shows  $\beta$  relaxation peak at -82°C and the  $\alpha$  relaxation peak corresponding to the  $T_g$  at 235°C. These data are used as reference and for comparing the data from the PPS/ATS blends.

The dynamic moduli and log  $\tan \delta$  plots are 90 PPS/10 ATS, 80 PPS/20 ATS, 70 PPS/30 ATS, and 60 PPS/40 ATS are shown in Figures 2-5, respectively. These figures show certain common features such as a gradual rise of log  $\tan \delta$  peaks to a maximum value and then leveling off. They also show a gradual drop of modulus. These figures indicate that blending of ATS has indeed lowered the glass transition temperatures in the PPS/ATS blends. The shift of  $T_g$  towards lower temperatures depends upon the weight proportion of ATS in the PPS/ATS blends. The plateau in the log  $\tan \delta$  curves beyond their peaks, demonstrate the reactive nature of ATS plasticizer. It has been shown by DSC scans that ATS has a  $T_g$  of 0°C and an exotherm initiating at 145°C which peaks at 245°C corresponding

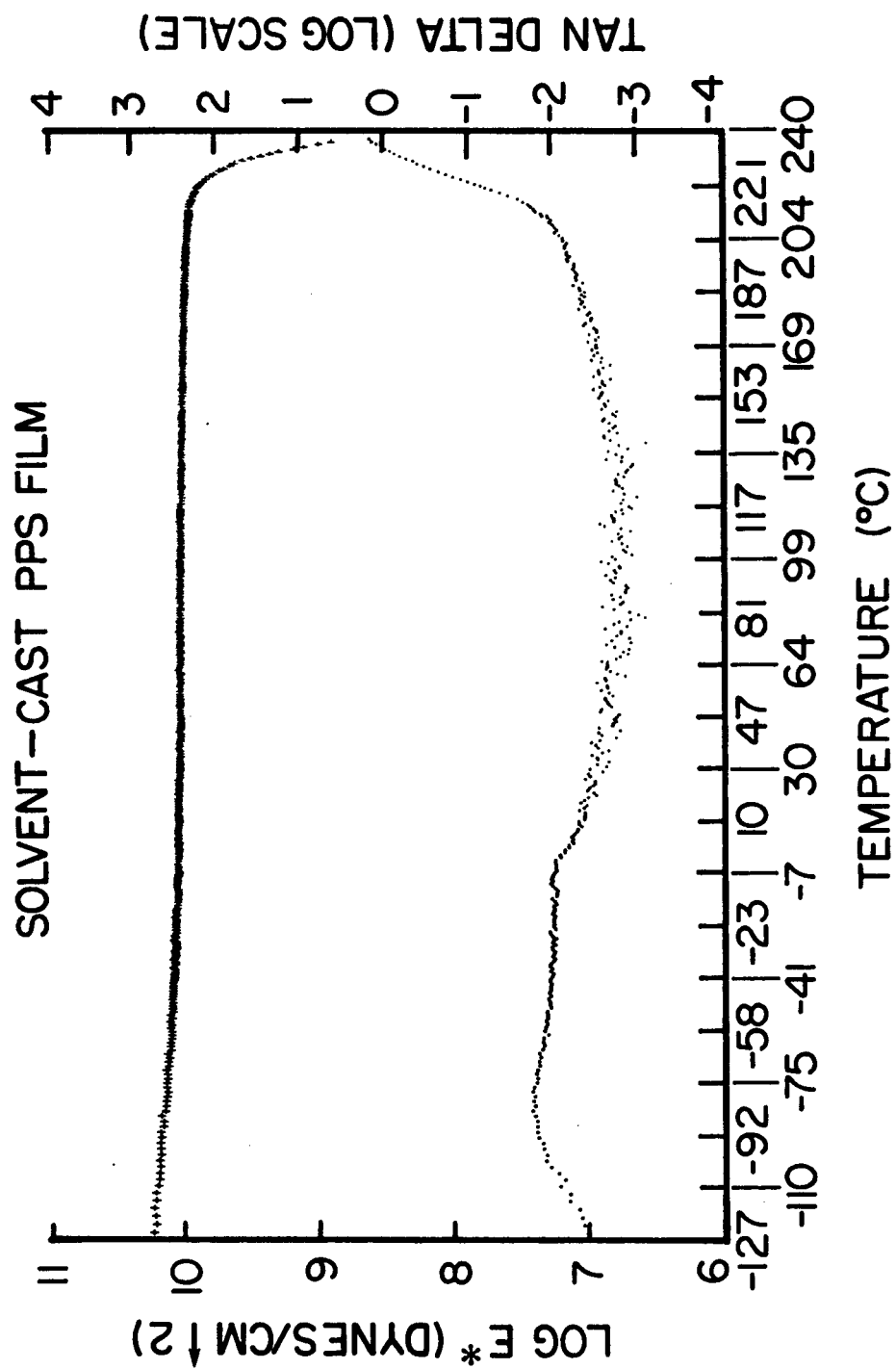


Figure 1. E\* and Log Tan  $\delta$  vs. Temperature Plot for Solvent Cast Polyphenylsulfone (PPS) Film

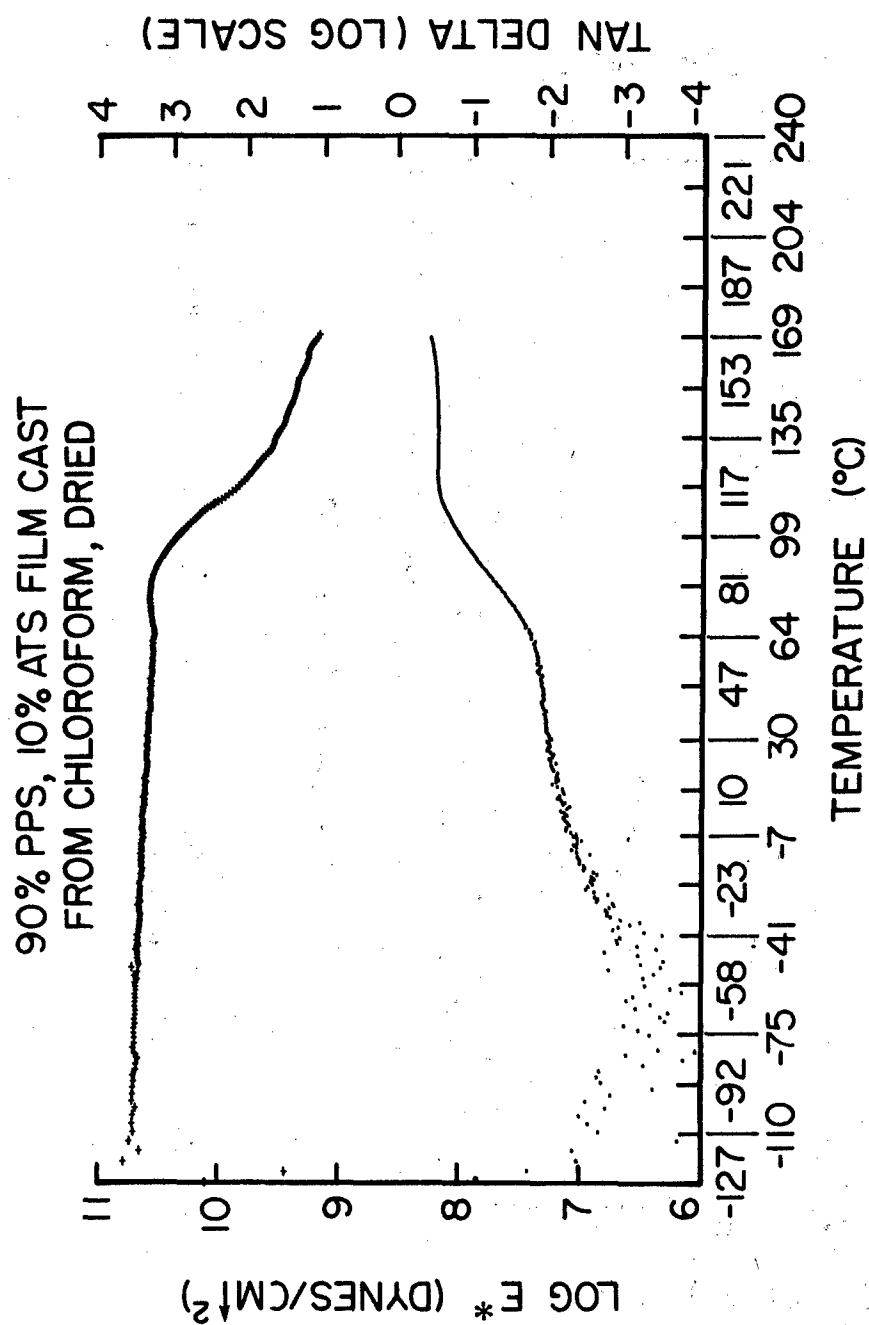


Figure 2. E\* and Log Tan  $\delta$  vs. Temperature Plot for 90 PPS/10 ATS  
Uncured Blend

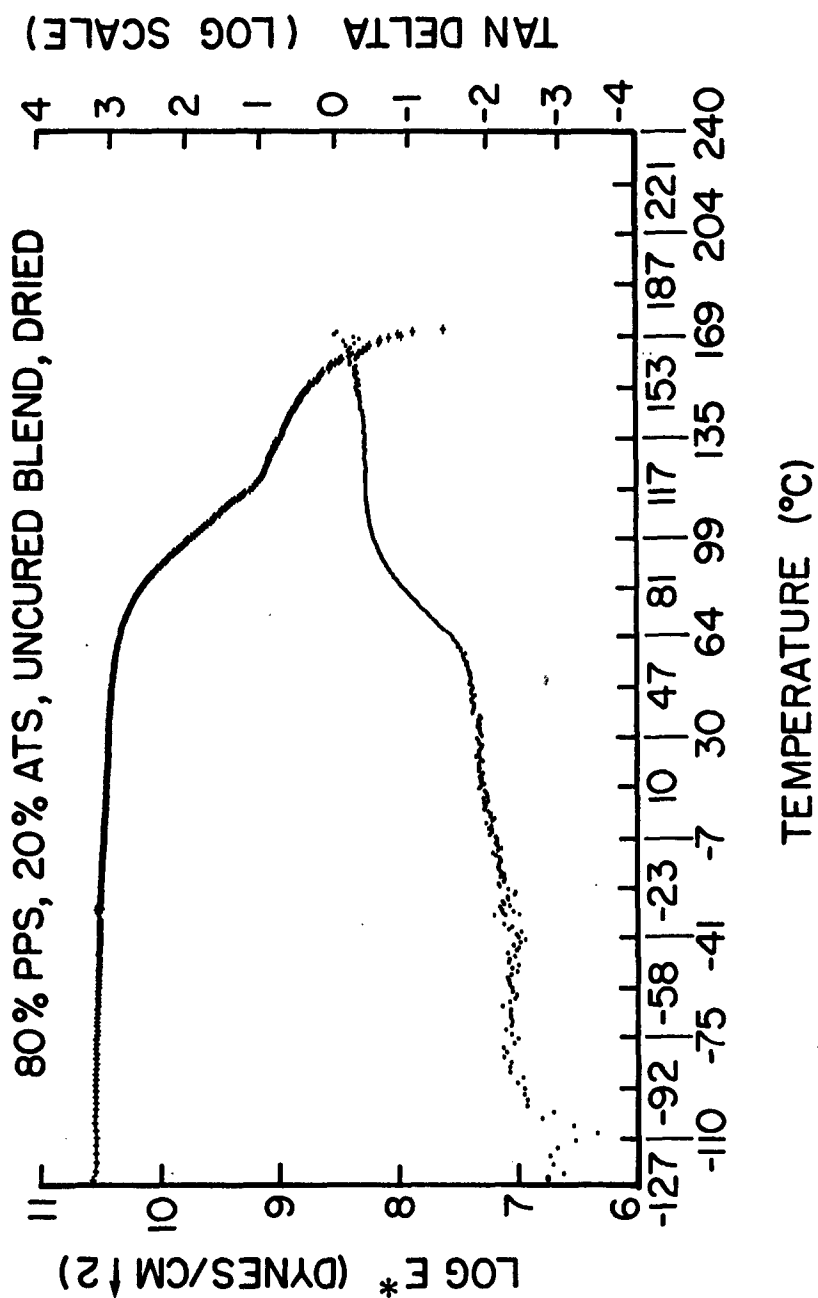


Figure 3. E\* and Log Tan  $\delta$  vs. Temperature Plot for 80 PPS/20 ATS Uncured Blend



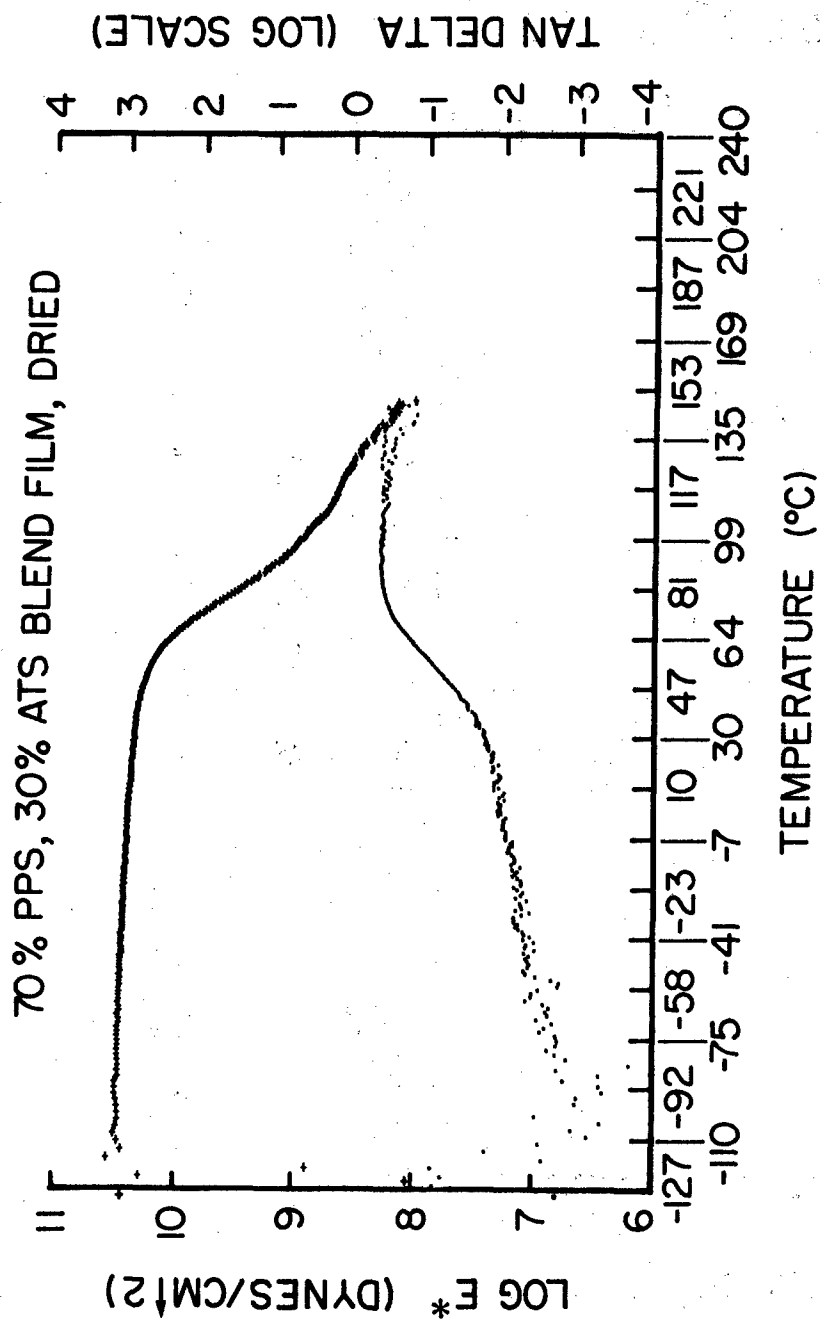


Figure 4. E\* and Log Tan  $\delta$  vs. Temperature Plot for 70 PPS/30 ATS Uncured Blend

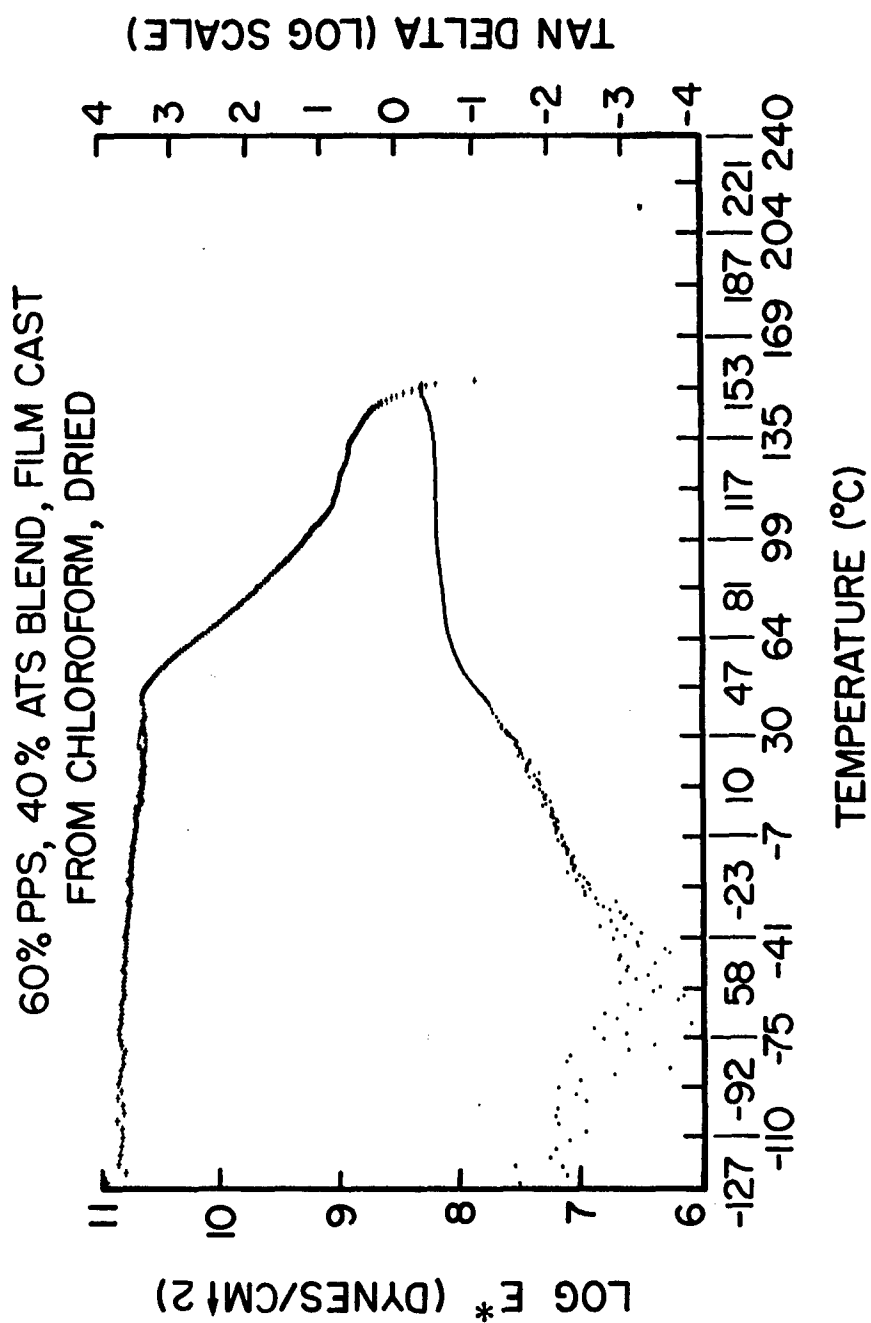


Figure 5. E\* and Log Tan  $\delta$  vs. Temperature Plot for 60 PPS/40 ATS  
Uncured Blend

to the polymerization reaction of ATS. Therefore, during a rheovibron scan, when the temperature is raised at a rate of  $\sim 2^{\circ}\text{C}/\text{minute}$ , the ATS in the polyblends reacts/crosslinks (above the  $T_g$  of polyblends) resulting in higher  $T_g$ s, as the blends are exposed to higher temperatures during the measurement. This behavior is evident in the  $\log \tan \delta$  vs. temperature plot of 90 PPB/10 ATS solvent-cast film shown in Figure 6. Here, Figure 6, curve 1 shows the first run made on the rheovibron and it shows a maximum at  $85^{\circ}\text{C}$ . This can be ascribed to the  $T_g$  of PPS/ATS blend where  $T_g$  may have been lowered more than expected because of the presence of solvent. The  $\beta$  relaxation peak in this scan is not observable because it may have been shifted to a much lower temperature than  $-85^{\circ}\text{C}$  where it has been observed for PPS alone. On rerunning this same specimen a second time after it has been exposed to  $200^{\circ}\text{C}$ , the peak corresponding to  $T_g$  shifts toward higher temperature (Figure 6, curve 2). Again a  $\beta$  relaxation peak is unobservable. On quenching and retesting the specimen, the maximum shifts toward still higher temperature (Figure 6, curve 3). The  $\beta$  relaxation peak begins to show up at  $-85^{\circ}\text{C}$ . Figure 6, curve 4 shows the  $\log \tan \delta$  peak from the 90 PPB/10 ATS film heated at  $121^{\circ}\text{C}$  for two hours under nitrogen (to remove solvent) and at  $275^{\circ}\text{C}$  for one hour. The rheovibron scan of this cured film (Figure 6, curve 4) shows a well-defined  $\beta$  relaxation peak as in PPS by itself (Figure 1). The  $T_g$  of the cured blend represented by an  $\alpha$  peak is  $220^{\circ}\text{C}$ , the same as the  $T_g$  of PPS polymer. This experiment clearly demonstrates the continuous shift towards higher temperatures of  $T_g$  due to increased crosslinking/curing of ATS. Since a sharp  $\log \tan \delta$  peak is not observable in dynamic mechanical data in Figures 2-5, the temperature at which  $\log \tan \delta$  approaches a maximum is taken as an onset of  $T_g$ . These  $T_g$ s seem to be representative of  $T_g$ s obtainable from loss moduli maxima as in Figure 7. The  $T_g$  of 80 PPS/20 ATS determined from  $\tan \delta$  peak is  $93^{\circ}\text{C}$  in comparison to  $T_g$  of  $88^{\circ}\text{C}$  from  $E''$  maximum in Figure 8. The  $T_g$  of various blends determined from  $\tan \delta$  peaks are given in Table 1.

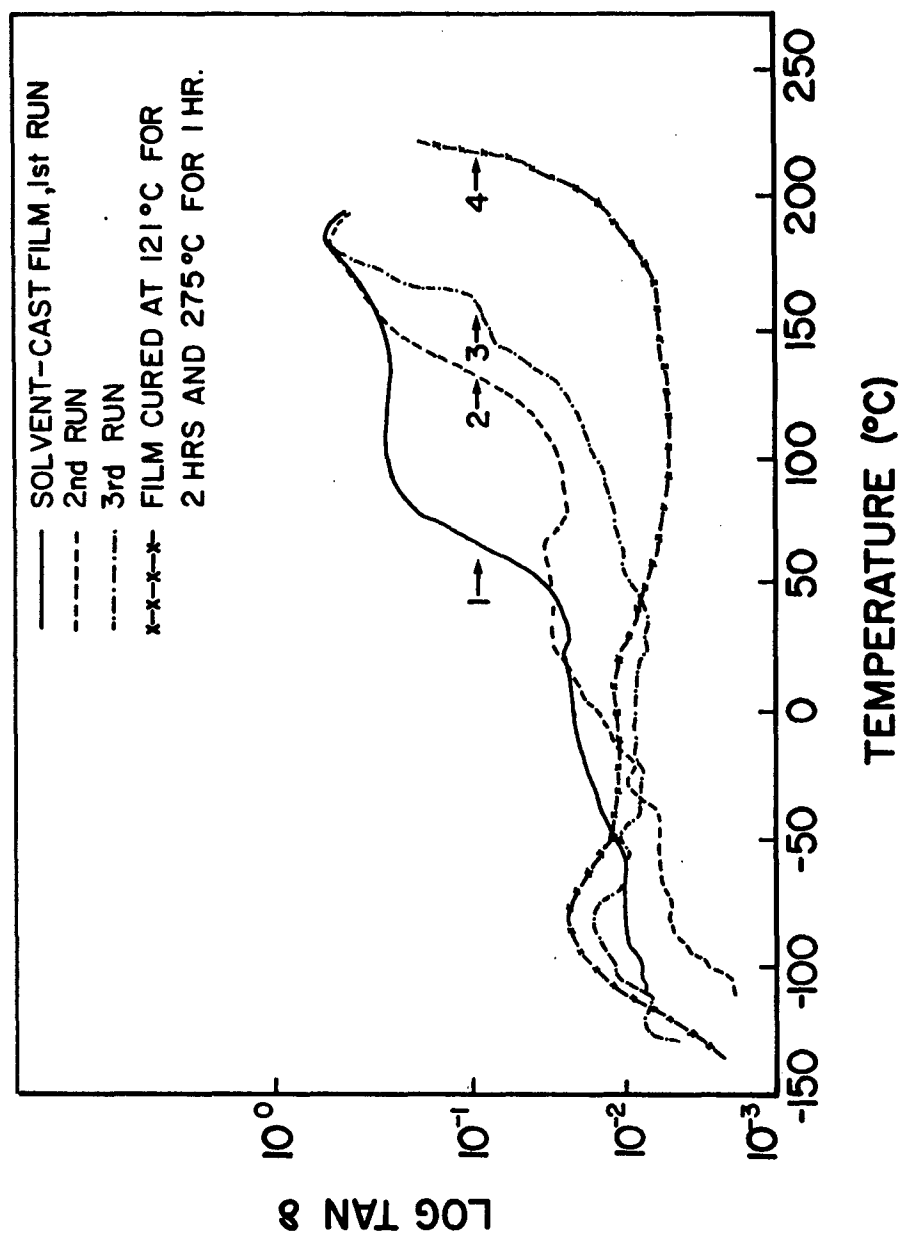


Figure 6. Log Tan  $\delta$  vs. Temperature Plot for 90 PPS/10 ATS  
Uncured Film

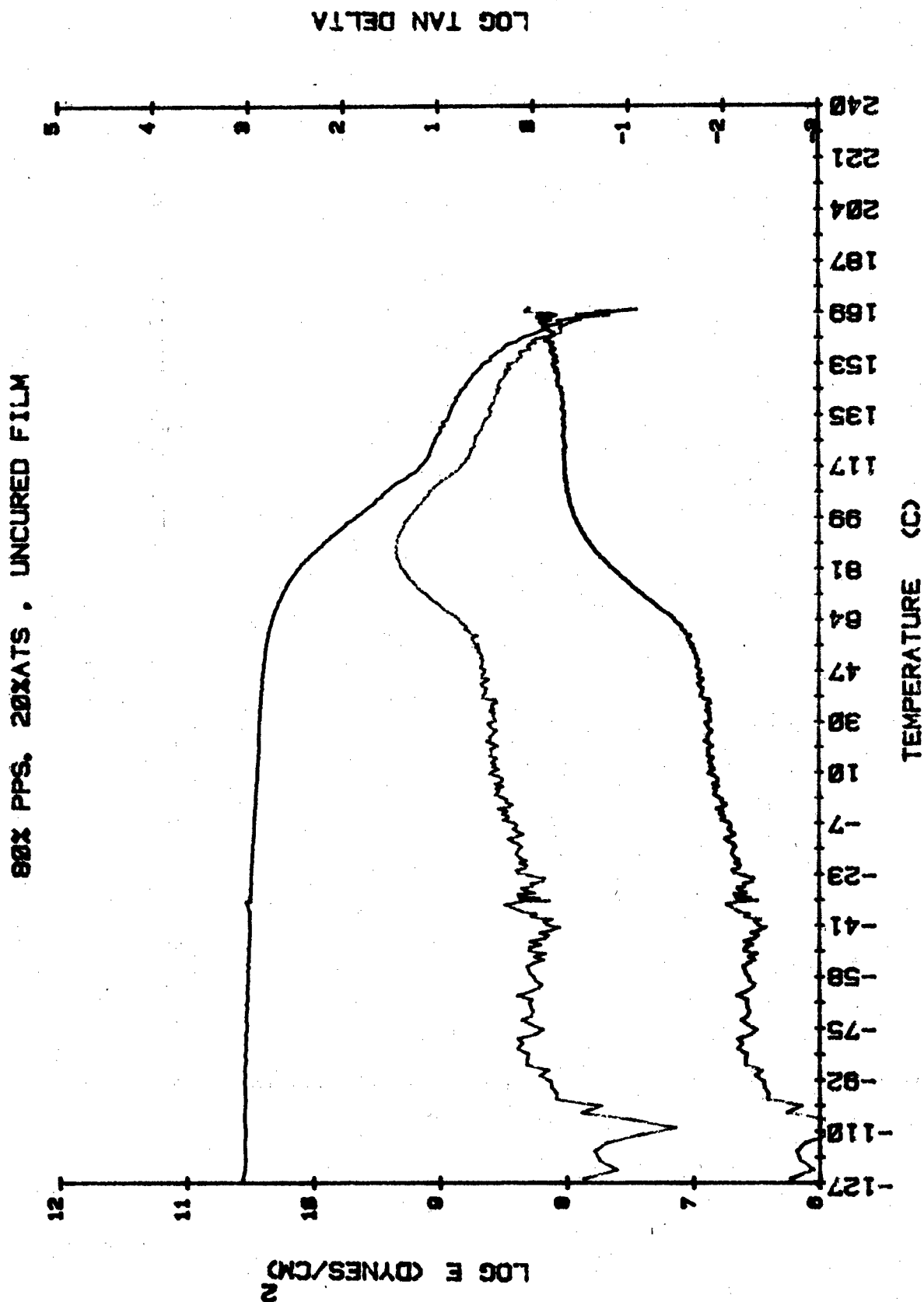


Figure 7. E', E'', and Log Tan  $\delta$  Plot of 80 PPS/20 ATS  
Uncured Blend

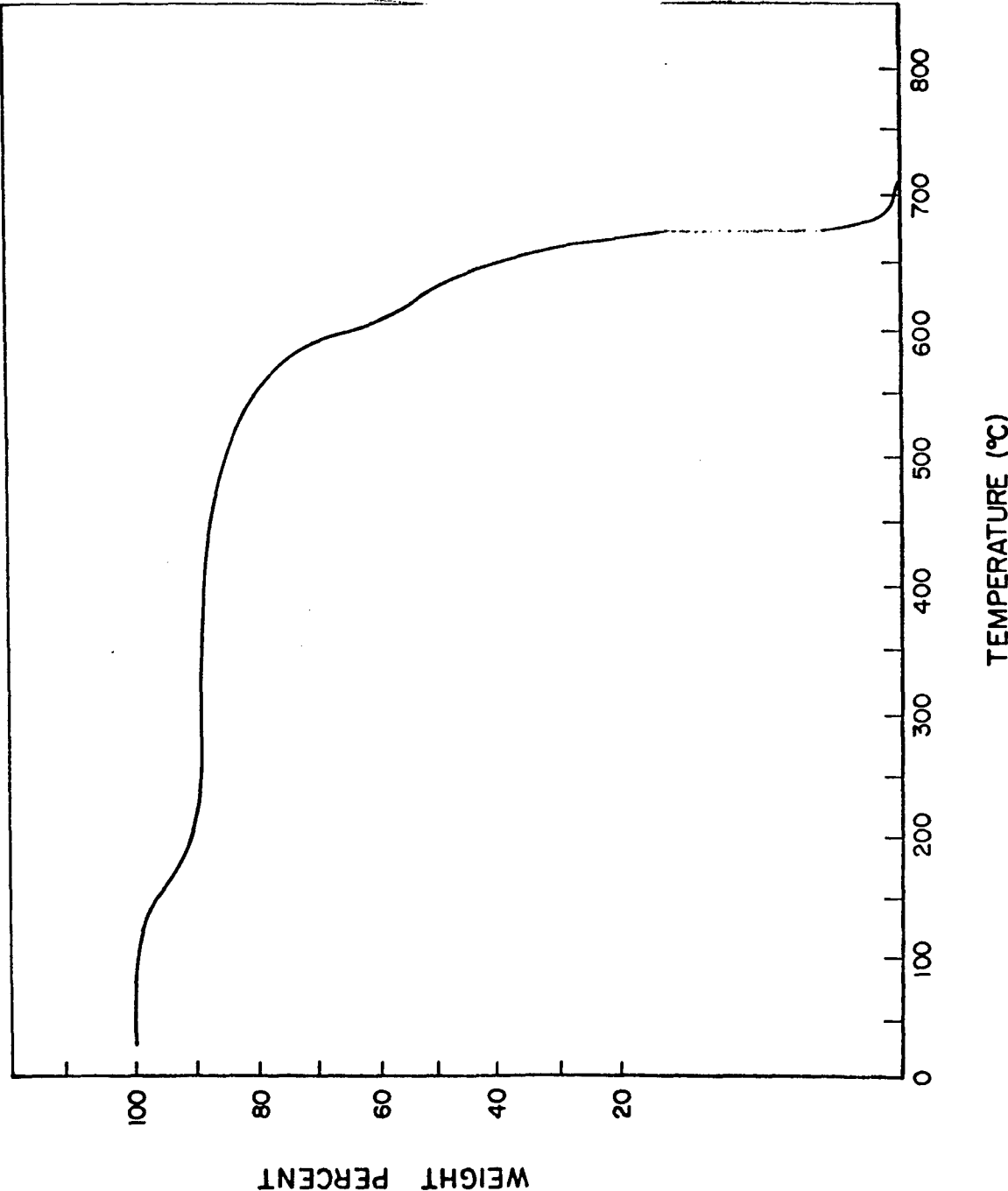


Figure 8. TGA Curve for 70 PPS/30 ATS Uncured Blend

TABLE 1  
OBSERVED & CALCULATED GLASS TRANSITION TEMPERATURES  
of PPS/ATS POLYBLENDS

WT % COMPOSITION IN BLENDS		WT % OF SOLVENT RETAINED IN THE BLEND	OBSERVED Tg BY RHEOVIBRON TESTS (°C)	CALCULATED Tg USING FLORY-FOX EQUATION (°C)	CALCULATED Tg USING KELLEY-BUECHE EQUATION (°C)
PPS	ATS				
100	0	5.9	235	--	188
90	10	13.0	108	194	125
80	20	13.8	93	160	98
70	30	14.6	75	130	75
0	100	8.5	0	--	--

TABLE 1 (Concluded)

OBSERVED & CALCULATED GLASS TRANSITION TEMPERATURES  
OF PPS/ATS POLYBLENDS

WT % COMPOSITION IN BLENDS		WT % OF SOLVENT RETAINED IN THE BLEND	OBSERVED Tg BY RHEOVIBRON TESTS (°C)	CALCULATED Tg USING FLORY-FOX EQUATION (°C)	CALCULATED Tg USING KELLEY-BUECHE EQUATION (°C)
PPS	ATS				
100	0	5.9	235	--	188
90	10	13.0	108	194	125
80	20	13.8	93	160	98
70	30	14.6	75	130	75
0	100	8.5	0	--	--



The data shown in this table includes calculated Tgs using the Flory-Fox equation as well as the Kelley-Bueche equation. The observed values are much lower than values calculated by using the empirical equation  $1/T_g = W_1/T_{g1} + W_2/T_{g2}$ . One reason for this disagreement is that the empirical relation is applicable to copolymers and here it has been applied to the polymer diluent system where diluent/plasticizer is of reactive type. Secondly, the solvent-cast films have been shown to retain solvent, as evident from Figure 8; TGA data on 70 PPS/30 ATS solvent-cast blend which displays 11% weight loss due to solvent. In addition, cure studies of these blends including weight losses and density measurements have also revealed retention of up to 14% solvent in the cast films (Table 2). Therefore, in addition to the plasticizing effect of ATS, solvent will further lower the Tgs. Consequently, the Tg's calculated by either of the above equations differ widely from the observed values. Therefore, the amount of solvent retained in the blends is taken into consideration in Tg calculations. This has been accomplished by including an additional term for the solvent in the Kelley-Bueche equation (Equation 1) for polymer - diluent systems (Reference 4). The modified equation is written as:

$$T_g = \frac{\alpha_p V_p T_{g_p} + \alpha_d (V_{d1} T_{g_{d1}} + V_{d2} T_{g_{d2}})}{\alpha_p V_p + \alpha_d (V_{d1} + V_{d2})} \quad (1)$$

where

$\alpha_p$  = coefficient of volume expansion of the polymer, assumed to be  $4.8 \times 10^{-4}$  per °C.

$V_p$  = Volume fraction of the polymer

$\alpha_d$  = Coefficient of volume expansion for the diluent/solvent assumed to be  $1 \times 10^{-3}$  per °C

$T_{g_p}$  =  $T_g$  of polymer = 220°C

$T_{g_{d1}}$  =  $T_g$  of ATS oligomer = 0°C

TABLE 2  
WEIGHT LOSS AND DENSITY CHANGES AS A FUNCTION OF CURE

POLYMER / BLEND	INITIAL DENSITY	CURED AT 80°C FOR 2 HOURS		CURED AT 150°C-180°C FOR 2 HRS		CURED AT 250°C FOR 2 HOURS		CURED AT 260°C-275°C FOR 2 HRS		CALC. DENSITY	TOTAL % WT. LOSS
		% WT. LOSS	DENSITY	% WT. LOSS	DENSITY	% WT. LOSS	DENSITY	% WT. LOSS	DENSITY		
80% PPS / 20% ATS	1.348	4.00	1.328	9.80	1.305	—	1.292	—	1.292	1.290	13.80
75% PPS / 25% ATS	1.345	5.15	1.325	8.30	1.300	—	1.287	—	1.291	1.290	13.45
70% PPS / 30% ATS	1.347	5.66	1.325	8.96	1.292	—	1.286	—	1.290	1.289	14.62
PPS	1.308*										
ATS	1.229	4.69		3.86		—		—	1.280		8.55

\*PPS  $\rho$  = 1.293 AFTER HEATING AT 220°C FOR 35 HOURS; % WT. LOSS = 5.9%

$T_{g_{d2}} = T_g$  of the solvent obtained by using Kelley-Beuche equation and substituting the observed  $T_g$  of 70 PPS/30 ATS.

$V_{d1}$  = Volume fraction of ATS

$V_{d2}$  = Volume fraction of solvent

$$V_p + V_{d1} + V_{d2} = 1$$

The  $T_g$ s thus calculated are included in Table 1. A good correlation exists between the calculated and observed  $T_g$ s of uncured blends when plasticizing effect of solvent is included in the  $T_g$  calculations.

The glass transition temperature of PPS and PPS/ATS blends were also determined by DSC and TMA. These are listed in Table 3. The DSC is less sensitive than thermomechanical analyzer (TMA) in the penetration mode to determine the  $T_g$ s of uncured blends. TMA shows penetration of the probe at more than one temperature. In the case of the 90 PPB/10 ATS blend, the penetration is observed at 62 and 152°C. In the 80 PPS/20 ATS blend, it occurs at 53 and 129°C (Figure 9) and for 70 PPS/30 ATS blend, it occurs at 34, 80 and 107°C. There are two possible explanations for this data. One, there is a possibility of separation in the blends into two phases; an ATS-rich PPS/ATS phase showing penetration at lower temperature and a PPS-rich PPS/ATS phase showing penetration at higher temperature. The TEM data tends to support this explanation. Second, since all cast films have been observed to contain residual solvent, it is possible that the first penetration may be due to the plasticizing effect of solvent where it begins to volatilize from the blend. In blends containing higher weight fraction of ATS, the softening occurs at even lower temperatures because the plasticization effect of solvent is augmented. The second penetration in these blends may actually be closer to the real  $T_g$  expected from the blends. Since all the solvent may not escape from the films, plasticization by solvent may still cause the observed  $T_g$  to be lower than calculated values based on Flory-Fox equation.

TABLE 3  
GLASS TRANSITION TEMPERATURE OF PPS AND PPS/ATS BLENDS AS  
DETERMINED BY DSC AND TMA

SAMPLE COMPOSITION	T <sub>g</sub> BY* TMA (°C)	CALCULATED** T <sub>g</sub> (°C)	T <sub>poly</sub> ONSET DETERMINED BY DSC (°C)	T <sub>poly</sub> PEAK DETERMINED BY DSC (°C)	T <sub>g</sub> OF SAMPLES*** CURED ON DSC (°C)
90 PPS/10 ATS	62 152	194	~195	255	215
80 PPS/20 ATS	53 129	160	~190	252	214
70 PPS/ 70 PPS/30ATS	34 80 107	130	~175	245	217
60 PPS/40 ATS	15	104	~175	244	215

1. HEATING RATE OF 10°C/MIN IS USED DURING THE DSC SCAN.

2. ALL FILMS ARE DRIED UNDER VACUUM FOR 8 DAYS.

\* TMA PROBE IS IN PENETRATION MODE

\*\* CALCULATED VALUES ARE BASED ON FLORY-FOX EQUATION

\*\*\* SAMPLES ARE HEATED TO 450°C AND KEPT AT THAT TEMP FOR 20 MIN BEFORE RESCANING ON DSC

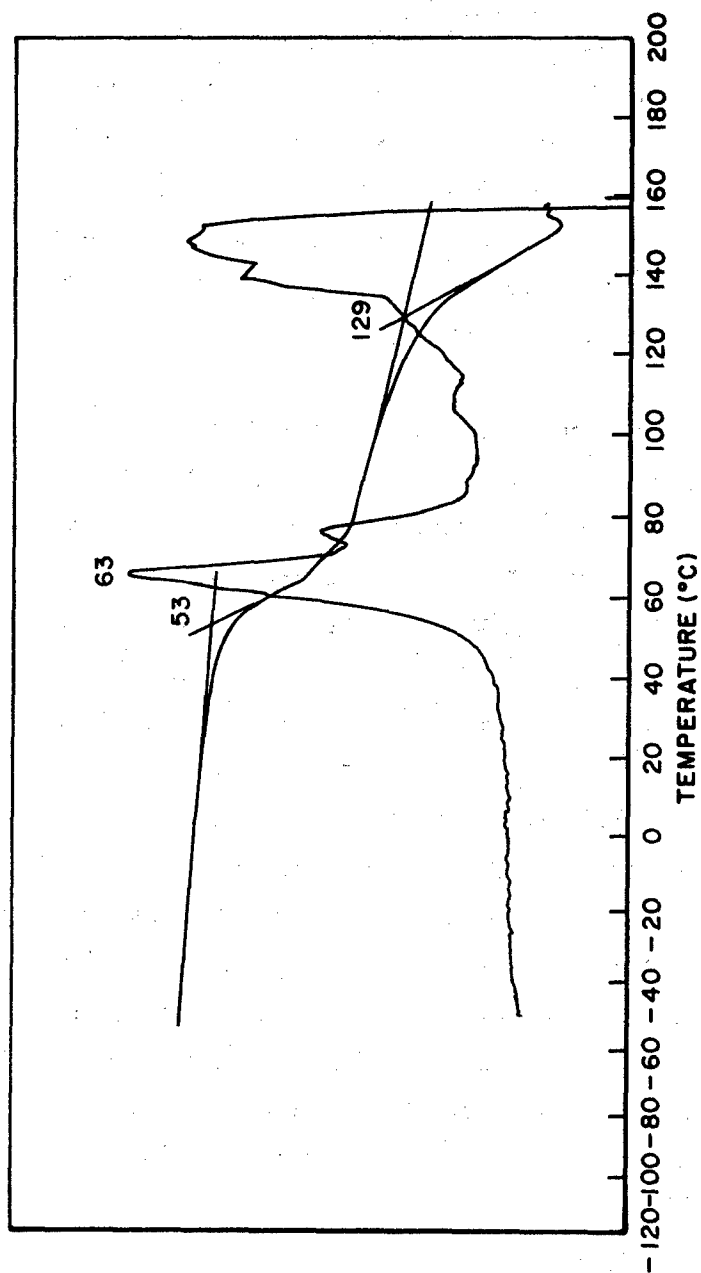


Figure 9. TMA Scan of 80 PPS/20 ATS Uncured Blend

In addition to the Tgs, Table 3 also shows onset and peak temperatures for reaction/polymerization of ATS indicated as " $T_{\text{poly}}$  onset" and " $T_{\text{poly}}$  peak", respectively. The Tgs of cured PPS/ATS blends in all cases have been observed to be 214-217°C. Figure 10 shows the DSC scans of uncured and cured 80 PPS/20 ATS blend. The sample cured on the DSC exhibits a single Tg at 214°C, which does not necessarily imply a single phase homogeneous blend because the crosslinked ATS, even if phase-separating from PPS, may not exhibit its own Tg. A DSC scan of "fully cured" ATS supports this argument as no Tg could be discerned from such a sample. Therefore, based on Tg data alone, it can not be concluded whether ATS phase separates on curing.

The Tgs shown in Table 3 are lower than the Tgs determined by rheovibron. This may be attributed to higher heating rate (of 10°C/min) in TMA and DSC as compared to a heating rate of 2°C/min in the rheovibron at a frequency of 11 Hz. The Tgs of cured blends determined by DSC are lower than the Tgs determined by rheovibron (Figure 11). This difference can be attributed to a different thermal history of the blends in the two experiments. In the case of DSC measurements, samples are heated at a heating rate of 10°C/min, up to 450°C and held there for 20 minutes, whereas the films tested on rheovibron are cured for a much longer time until the  $3280\text{ cm}^{-1}$  IR band (assigned to C-H stretching mode of  $\text{RC}\equiv\text{CH}$  groups) disappears. The Tgs of uncured and cured blends as observed by DSC and TMA along with calculated Tgs are plotted in Figure 12. It is evident from this figure that the calculated Tgs of all blends using the Flory-Fox equation are higher than the observed Tgs. This can be due to the residual solvent in observed samples which has not been taken into account in the Tg calculation. The Tgs of cured blends remain constant at 215°C.

A series of DSC scans of "fully cured" 80 PPS/20 ATS films (cured in the vacuum oven until the  $3280\text{ cm}^{-1}$  band disappears) have been taken and are shown in Figure 13. It is interesting to note that the Tg of

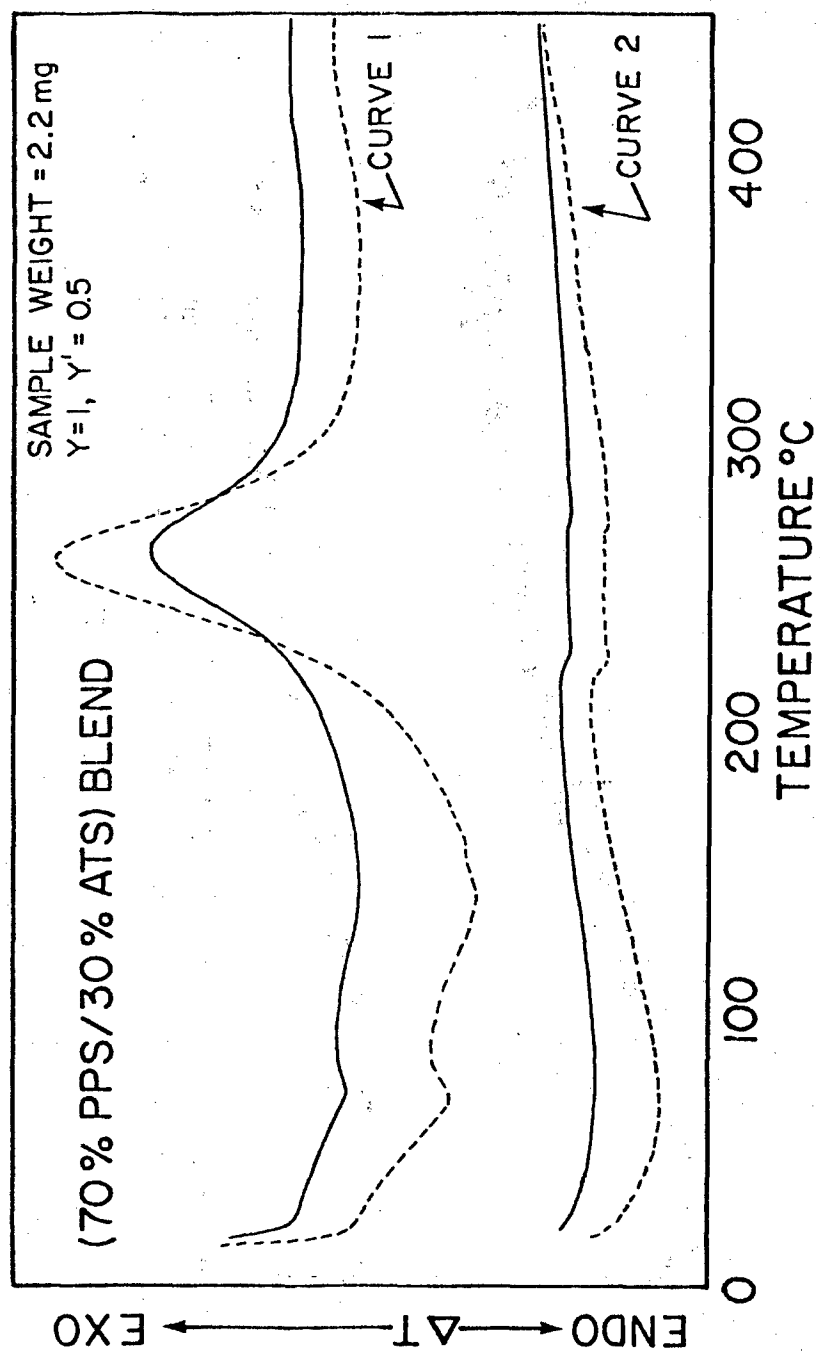


Figure 10. DSC Scan of 80 PPS/20 ATS Cured Blend

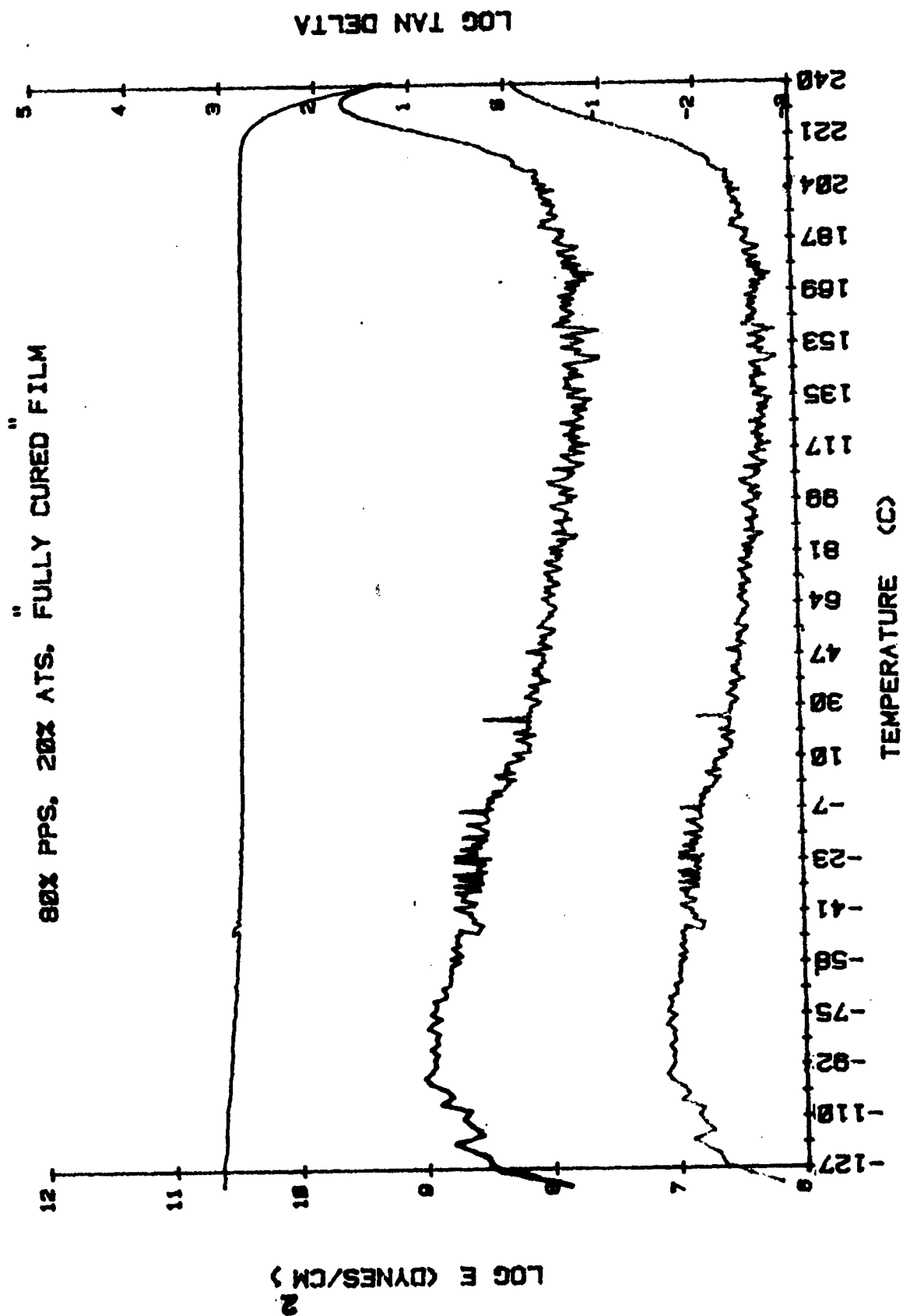
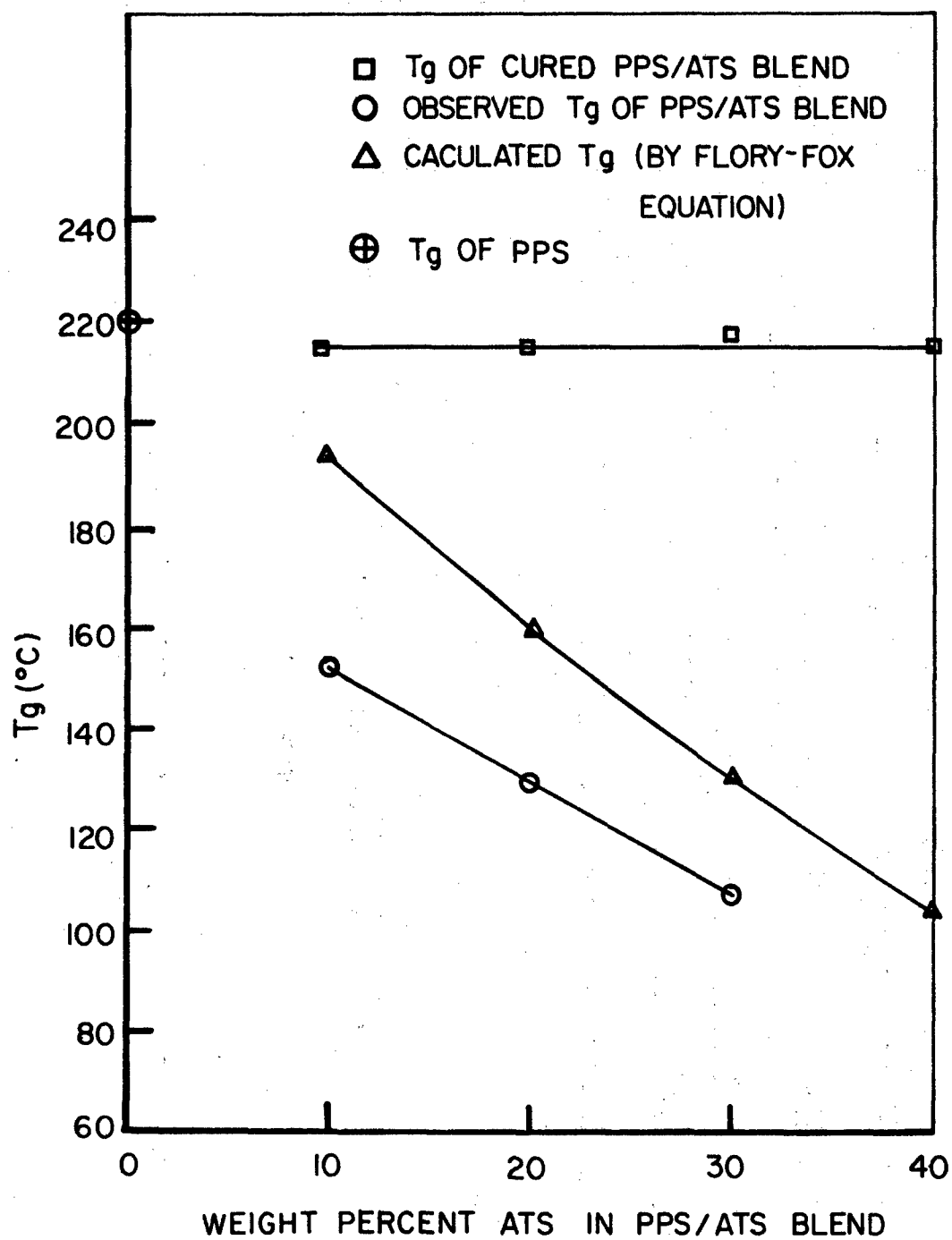


Figure 11. E', E'', and Log Tan  $\delta$  vs. Temperature Plot for 80 PPS/  
20 ATS "Fully Cured" Blend



Figure 12. Plot of  $T_g$ 's of Uncured and Cured Blends

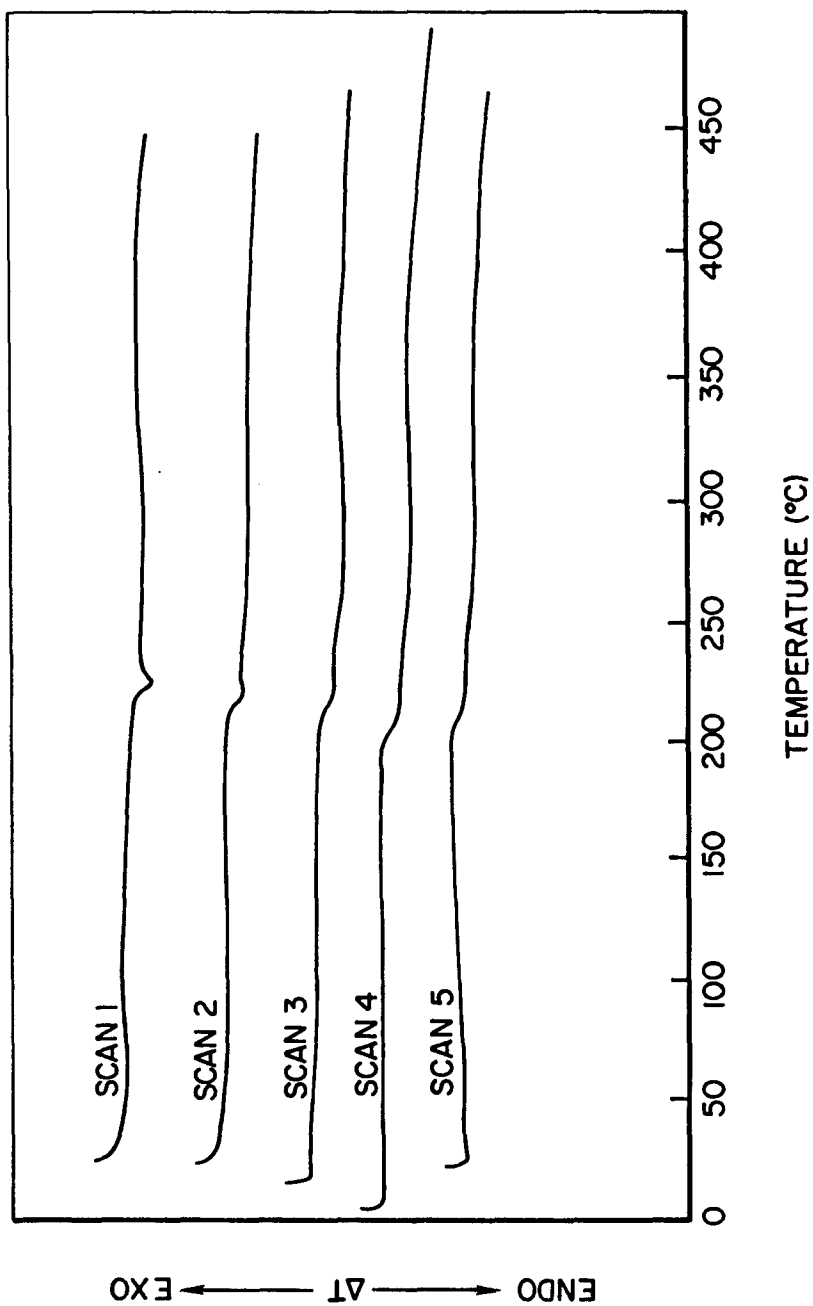


Figure 13. DSC Scans of 80 PPS/20 ATS "Fully Cured" Blend

80 PPS/20 ATS "fully cured" blend is 221°C during the first scan, which is higher than 215°C, previously observed from samples cured on DSC. This DSC scan also does not show a second T<sub>g</sub> due to ATS. Of course, it is possible that the T<sub>g</sub> of highly crosslinked ATS may not be observable, as discussed previously. Another interesting feature of this figure (that needs explanation) is the broadening and shifting of T<sub>g</sub> toward lower temperature on repeated scans. This could be due to degradation of PPS on repeated heating to 450°C which deserves further investigation.

## 2. CURING OF PPS/ATS BLENDS

Since solvent-cast films of the blends retain solvent, it is necessary to degas the films before curing. It has been observed that the blends cured in a preheated oven showed numerous bubbles/voids whereas the blends placed in the oven at room temperature and heated up in various stages do not foam or exhibit voids. Therefore, films have been heated for two hours at 80°C, essentially, to remove the trapped solvent followed by cure for two hours at 150-180°C and four hours at 250°C. Infrared spectra of blends cured at 80°C (150-180°C and 250°C) are obtained. A superimposed IR spectra of uncured and "fully cured" 80 PPS/20 ATS are shown in Figure 14. It shows disappearance of the 3280 cm<sup>-1</sup> and 3428 cm<sup>-1</sup> IR bands and a decrease in the intensity of the 935 cm<sup>-1</sup> IR band when cured up to 250°C for four hours. Additional cure time and/or temperature shows no further change in the IR spectrum of cured blends. The 3428 cm<sup>-1</sup> IR band is assigned to O-H stretch which seems to be due to water absorbed in the PPS and ATS. This band decreases in intensity as the PPS/ATS blend is heated for two hours at 80°C and for two hours at 150-180°C. The 3280 cm<sup>-1</sup> IR band is assigned to the C-H stretch of the -C≡CH group present in the ATS (Reference 5). This 3280 cm<sup>-1</sup> band does not decrease in intensity unless the PPS/ATS blend is cured at 150-180°C but it does disappear when the blend is cured for four hours at 250°C indicating addition reaction and conversion of acetylene groups to form a polyene. It is observed that the 935 and

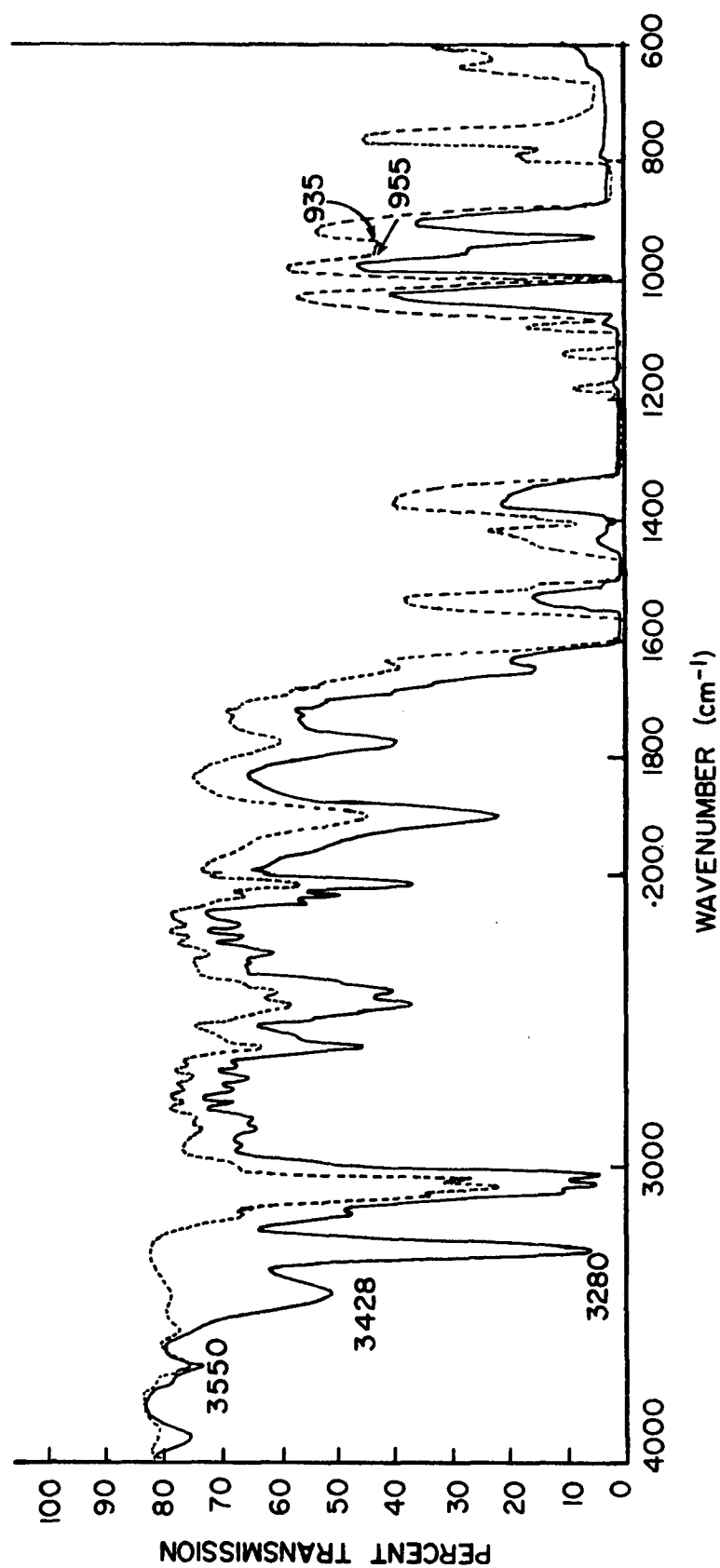


Figure 14. Superimposed IR Spectra of Uncured and Cured 80 PPS/20 ATS Blend

955  $\text{cm}^{-1}$  doublet has the same intensity in the IR spectrum of PPS film. However, the intensity of the 835  $\text{cm}^{-1}$  band is greater in the IR spectrum of ATS alone and this shows up in the spectrum of the PPS/ATS blend. The 935  $\text{cm}^{-1}$  band also decreases in intensity on curing of PPS/ATS blends for four hours at 250°C suggesting that this band must be related to the C-H deformation associated with the  $-\text{C}\equiv\text{C}-\text{H}$  group.

### 3. VISCOSITY MEASUREMENTS

Figure 15 shows the log viscosity vs. temperature for PPS polymer obtained from the Rheometrics instrument using parallel plates (Reference 6). The viscosity of PPS is above  $10^6$  poise at 250°C. Figure 16 shows log  $\eta$  vs. temperature plot for 80 PPS/20 ATS polyblend. The viscosity for this blend is  $5 \times 10^5$  poise at 130°C and remains so up to 180°C when ATS begins to react and the viscosity starts to increase. The viscosity of 70 PPS/30 ATS, shown in Figure 17, drops to  $3 \times 10^5$  poise at 125°C and it further decreases until 180°C before it starts to increase due to polymerization and crosslinking of ATS.

Thus, addition of ATS to PPS polymer lowers its viscosity and the polyblends are processable at 180°C as opposed to temperatures of 300°C or higher needed to process PPS polymer.

### 4. SOLVENT/CHEMICAL RESISTANCE

"Fully cured" blends as evidenced by the disappearance of 3280  $\text{cm}^{-1}$  film, were tested for their resistance towards solvents usually encountered in the maintenance and operation of aircraft. The time to fracture PPS and 80 PPS/20 ATS thin films, while under 500 psi stress and in contact with four different solvents/chemicals, are compared in Table 4. The PPS/ATS blends show improved resistance toward solvents than PPS by itself. The data for PPS has been obtained by running chemical resistance tests on 10 mil thick commercial films as opposed to ~ 3 mil thick cured 80 PPS/20 ATS films. Therefore, even minor flaws, cracks and voids in the cured PPS/ATS blend films will accelerate solvent effect much more than tiny

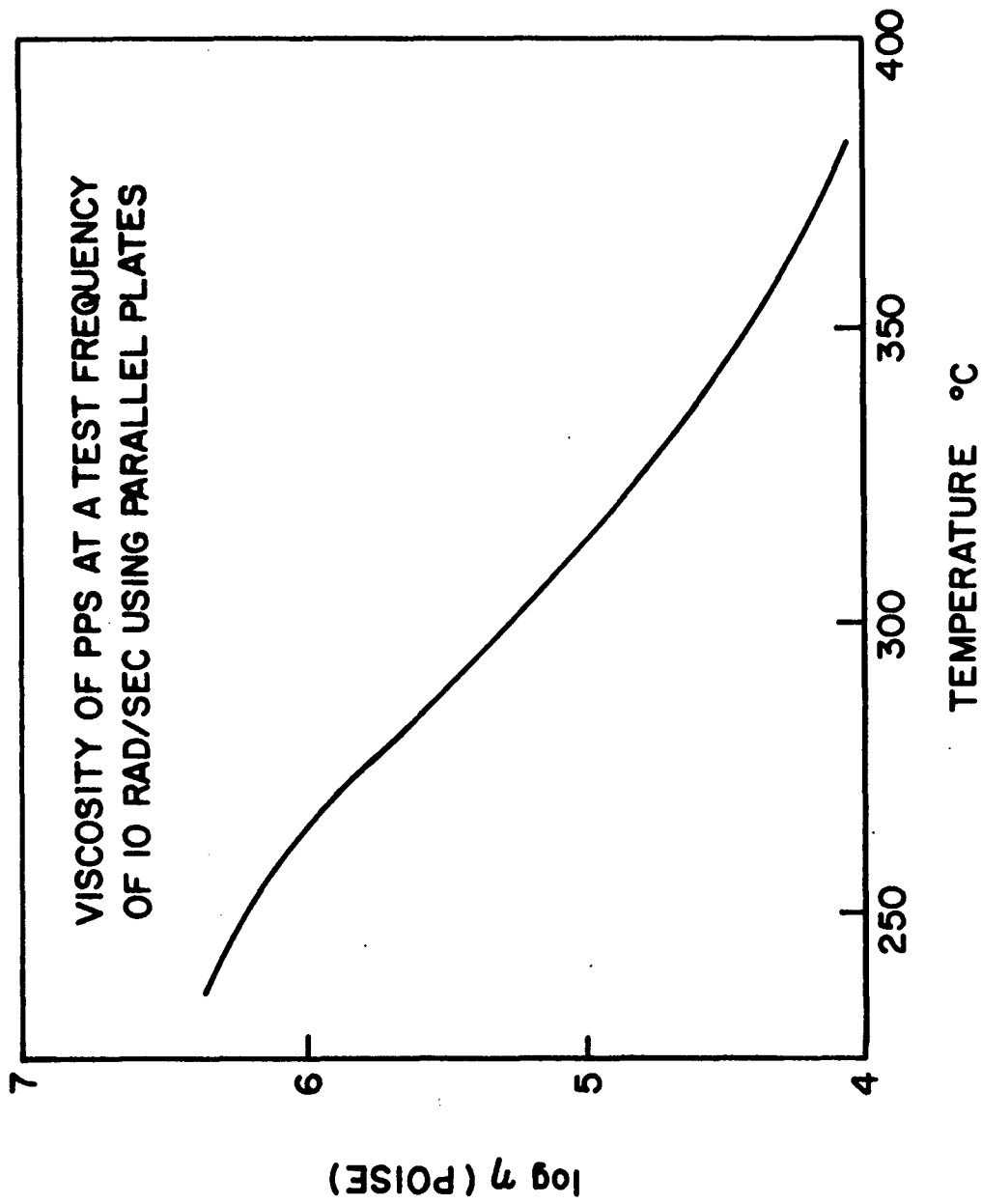


Figure 15. Viscosity vs. Temperature Plot for PPS Polymer Film.  
Test Frequency = 1.6 HZ

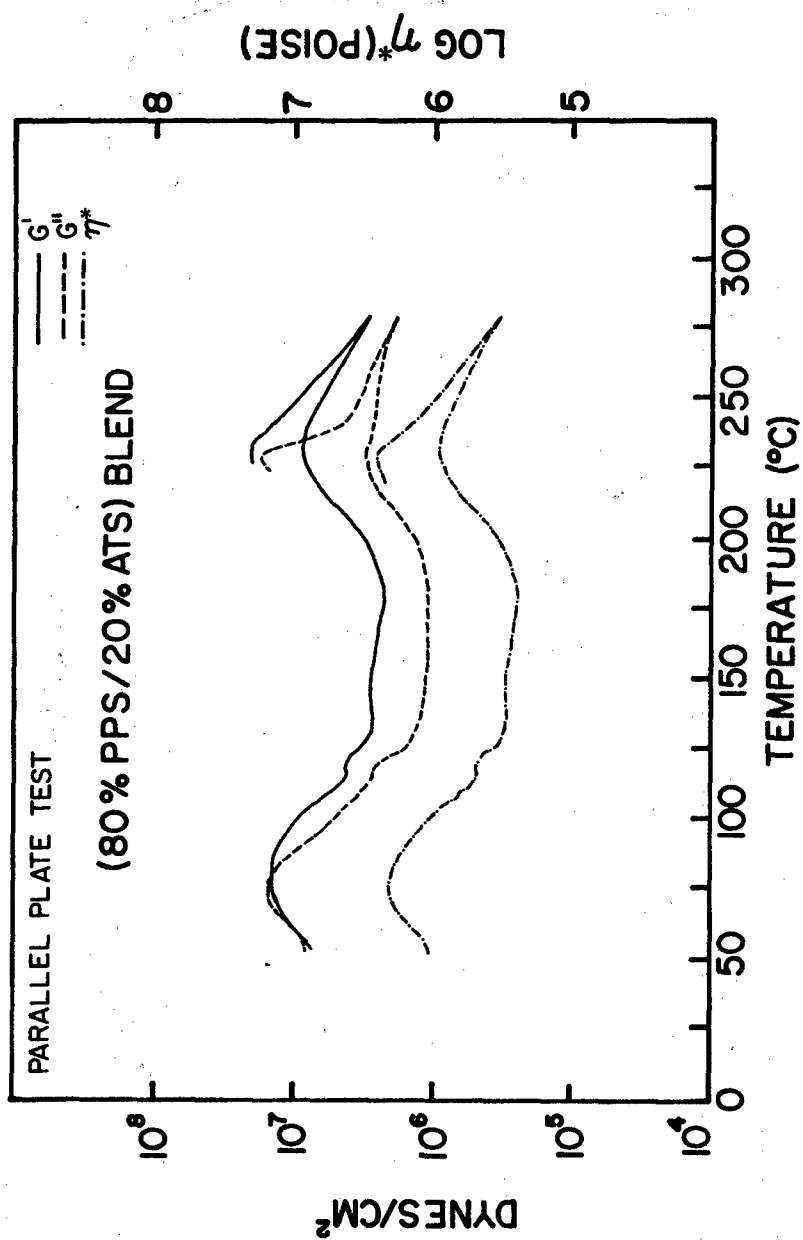


Figure 16. Viscosity vs. Temperature Plot for 80 PPS/20 ATS Uncured Blend. Test Freq. = 1.6 HZ

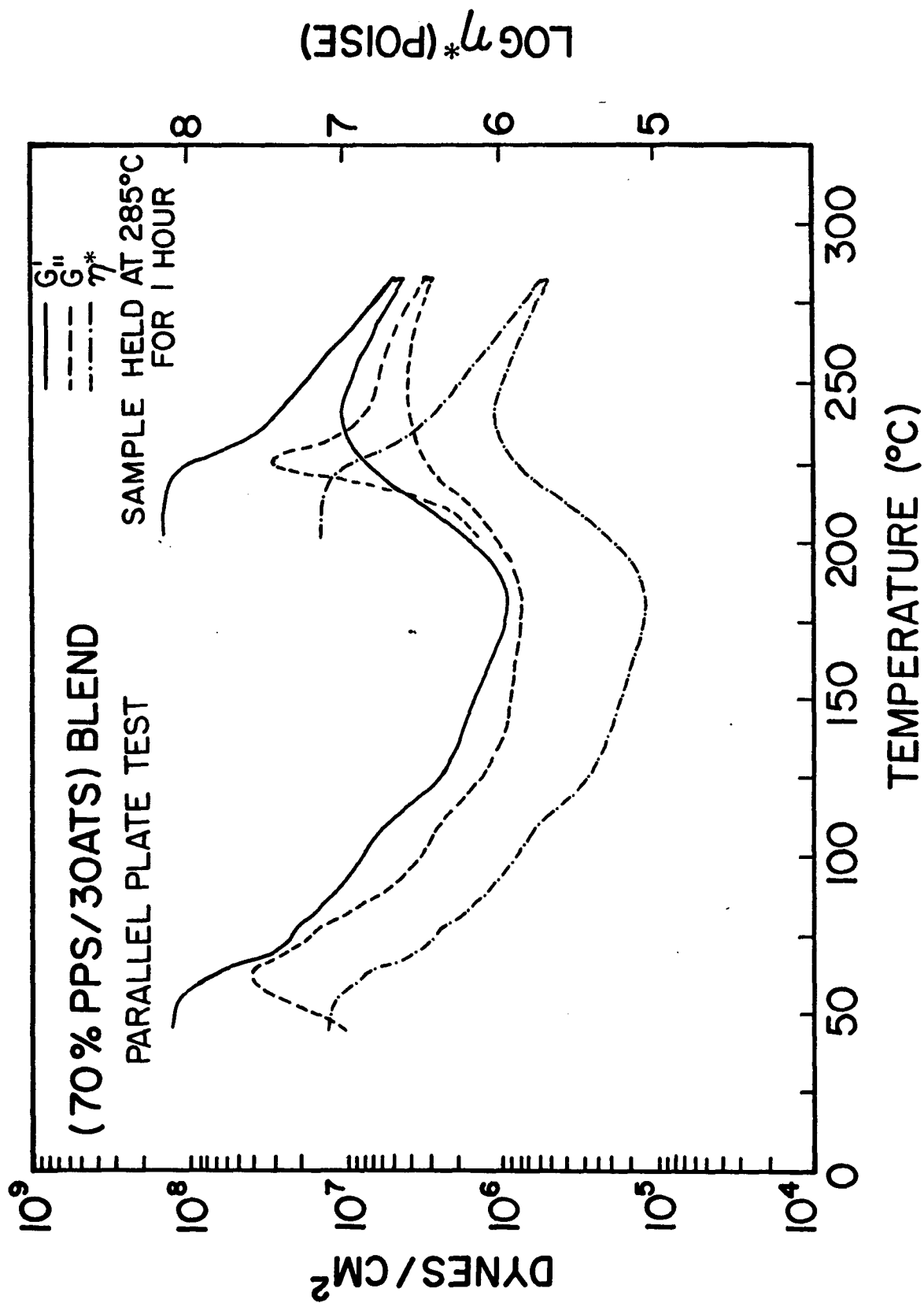


Figure 17. Viscosity vs. Temperature Plot for 70 PPS/30 ATS Uncured Blend. Test Freq. = 1.6 HZ



TABLE 4  
 SOLVENT RESISTANCE OF PPS AND "FULLY CURED"  
 80 PPS/20 ATS POLYBLEND

SAMPLE RUPTURE TIME UNDER 500 PSI STRESS IN				
POLYMER/ BLEND	AGENT	AGENT	AGENT	AGENT
	MEK	DICHLOROMETHANE	PAINT STRIPPER	SKYDROL 500B
*PPS FILM	1 sec	1 sec	4 min	4 min
80% PPS/ 20% ATS FULLY CURED FILM	5 min	5 min 39 sec	24 min	4 <u>hours</u>

\*TEST CONDUCTED ON 10 ml THICK COMMERCIAL PPS FILM

cracks, flaws, and voids in 10 mil thick films. Nevertheless, the data in Table 4 shows that PPS film blended with ATS can withstand solvents for much longer time. It is expected that 10-15 mil thick blended films would resist failure due to their contact with solvent for longer time than thin films tested in the present case.

Solvent-crazing and failure of amorphous thermoplastics under stress is known to occur by diffusion of organic solvents. In case of PPS/ATS blend, ATS polymerizes and crosslinks on curing providing an interpenetrating network structure with PPS. Such a molecular structure would reduce the rate of diffusion of the solvents and also provide structural integrity (due to crosslinks) even if PPS is attacked by the solvent.

## SECTION IV

### CONCLUSIONS

The data presented in this report does not support the existence of a totally homogeneous single-phase PPS/ATS polyblend. There are indications that these blends may indeed separate into PPS and ATS rich phases, forming domains of the order of 0.5 to 1  $\mu\text{m}$ , in both the uncured and cured state.

The Tgs of "fully cured" blends are observed to be equal to or greater than the Tg of PPS thermoplastic. Of course, the Tg of ATS may not be evident but is expected to occur above 220°C.

Solvent-cast polyblend films of PPS/ATS retain about 14% solvent which has additional influence in lowering Tgs in the uncured state. Therefore, curing of PPS/ATS blends needs to be carried out in stages such that the temperature is raised gradually to prevent foaming and void formation. The Tgs calculated by including solvent contribution to the Kelley-Bueche equation for polymer-diluent systems agree well with the observed Tgs. The Tgs of uncured blends calculated by using the Flory-Fox equation are higher than the Tgs observed by Thermal Mechanical Analyzer.

The complex viscosities of PPS/ATS uncured blends, determined in parallel plate mode, are lower than those of PPS. Therefore, PPS/ATS blends can be processed at lower temperatures.

"Fully cured" PPS/ATS blends show improved resistance toward organic solvent than PPS polymer alone.

REFERENCES

1. G. A. Loughran and F. E. Arnold, Polymer Preprints, 21, No. 1, 199 (1980).
2. Union Carbide Document No. F-4624 (Oct, 1976).
3. D. W. Van Krevelen and P. J. Hoftyzer, "Properties of Polymers, Their Estimation and Correlation with Chemical Structure," Elsevier Scientific Publishing Co., New York, 1976, pp. 216.
4. F. N. Kelley and F. Bueche, J. Poly. Sci., 50, 549 (1961).
5. N. L. Alpert, W. E. Keiser, H. A. Szymanski, "IR-Theory and Practice of Infrared Spectroscopy," Plenum, New York, 1970, pp. 260.
6. C. Y. - C. Lee, J. D. Henes, and T. E. Grossman, AFML-TR-79-4069, Wright-Patterson Air Force Base, Ohio 45433, Jan. (1980).